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Electronic states and nature of bonding in the molecule YC by all electron *ab initio* multiconfiguration self-consistent-field calculations and mass spectrometric equilibrium experiments

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In the present work we present results of all electron *ab initio* multiconfiguration self-consistent-field calculations of eight electronic states of the molecule YC. Also reported are the calculated spectroscopic constants. The predicted electronic ground state is $^4\Pi$, but this state is found to be separated from a $^2\Pi$ state by only 225 cm^{-1}, and by 1393 cm^{-1} from a $^2\Sigma^+$ state. The chemical bond in the $^4\Pi$ ground state is mainly due to the formation of a bonding molecular orbital composed of the $4d\pi$ of Y and the $2p\pi$ on C. The $5s$ electrons of Y are partly transferred to the $2p\sigma$ orbital on C, and they hardly contribute to the bonding. The chemical bond in the YC molecule is polar with charge transfer from Y to C giving rise to a dipole moment of 3.90 D at 3.9 a.u. in the $^4\Pi$ ground state. Mass spectrometric equilibrium investigations in the temperature range 2365–2792 K have resulted in the dissociation energy $D_0^\circ = 414.2 \pm 14$ kJ mol^{-1} for YC(g), and a standard heat of formation $\Delta H_{f,298.15}^\circ = 708.1 \pm 16$ kJ mol^{-1}.

I. INTRODUCTION

Transition metals and their alloys are essential components in heterogeneous catalysts used in technological processes and applications involving carbon containing gases. Studies of small units containing a carbon and a transition metal atom, that is diatomic transition metal carbides, are thus of considerable scientific and technological interest.

The present paper has been devoted to the yttrium carbide molecule. The theoretical and experimental investigations of this molecule have been part of our ongoing research on diatomic transition metal carbide molecules.[1–7]

For the diatomic carbide molecules of the second transition metal series, high temperature equilibrium measurements have shown that the dissociation energies, D_0° of the end members, PdC and YC are consistently smaller than those measured for NbC (564 ± 13 mol^{-1}), MoC (478 ± 16 kJ mol^{-1}),[8] RuC (612.1 ± 10.5 kJ mol^{-1}),[5] and RhC (576.0 ± 3.8 kJ mol^{-1}),[2] namely $\leqslant 430 \pm 20$ kJ mol^{-1} for PdC[1] and $\simeq 417$ kJ mol^{-1} for YC.[4]

Spectroscopic investigations of RhC[9] have shown the electronic ground state to be $^2\Sigma^+$, whereas the spectroscopic investigations of RuC could not assign the symmetry of the electronic ground state.[9]

Theoretical investigations have been performed for the platinum metal triad mono carbides RuC,[3,5] RhC,[2,3] and PdC.[1,3,10] Besides confirming the $^2\Sigma^+$ symmetry of the electronic ground state of RhC, these investigations have predicted the electronic ground state of the RuC molecule to be $^3\Delta$, and that of PdC as $^3\Sigma^-$.

It appears that the major reason for the remarkable differences between the bond energies of RhC and RuC as compared to those of PdC and YC are related to the atomic orbital configurations of the transition metal atoms. The ground term configurations of the atoms Rh and Ru are $(4d)^8(5s)^1$ and $(4d)^7(5s)^1$, respectively. The *ab initio* calculations of the carbide molecules, RhC[2] and RuC,[4] have revealed that each molecule is multiply bonded due to the involvement of the open $4d$ orbitals, while the $5s$ orbital is essentially nonbonding. The Pd atom has a $(4d)^{10}$ ground term configuration and that of Y is $(4d)^1(5s)^2$. Thus, in the Pd atom the $4d$ shell is fully occupied while the open $4d$ shell in the Y atom is shielded by the fully occupied $5s$ orbital, and therefore the $4d$ orbitals of neither atoms, Pd and Y, are easily accessible to the bond formation.

The results of the *ab initio* calculations for the molecule PdC[1] have shown that the chemical bond in this molecule can be explained in terms of donation and back donation of charge. In this connection it is especially interesting to investigate the nature of the chemical bond in the YC molecule. Since the $5s$ orbital of the Y atom is filled, the $4d$ electron of Y can only be involved in the formation of the chemical bond if part of the $5s$ electrons of Y are removed. This can occur by charge transfer from Y to C, or by the $5s$ electrons of Y occupyng a nonbonding molecular orbital in YC as is the case for the molecules RuC and RhC.

In the present investigation we report results of *ab initio* calculations and high temperature equilibrium measurements for the molecule YC. To our knowledge there are no previous theoretical calculations performed for this

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molecule. Previous high temperature mass spectroscopic measurements on gaseous yttrium carbides[11–13] have attributed the observed YC^+ ion to a fragment product, predominantly from YC_2, on basis of the observed high value of its appearance potential: 13.4 ± 0.5 eV,[11] 14.0 ± 1 eV,[12] and 13.5 ± 1.0 eV.[13] In Ref. 13, Gingerich and Haque also report a small tail at the low energies of the ionization efficiency curve of YC^+ with an appearance potential of 8 ± 2 eV that suggested the presence of trace amounts of primary YC^+. On the basis of this information we have later estimated a dissociation energy of approximately 417 kJ mol^{-1} for the YC molecule.[4]

The low-lying electronic states of the YC molecule have been studied by performing all electron *ab initio* Hartree–Fock (HF) and multiconfiguration self-consistent-field (MCSCF) calculations. The HF calculations have been carried out in the Hartree–Fock–Roothaan formalism.[14] The integrals have been computed using the program MOLECULE,[15] and for the HF calculations we have utilized the ALCHEMY program system.[16] The MCSCF calculations have been performed using the CASSCF program.[17–20]

II. THEORETICAL INVESTIGATIONS OF THE YC MOLECULE

A. Basis sets and HF calculations on C, Y, and YC

The basis sets consisted of contracted Gaussian-type functions. For the Y atom the basis set is essentially Huzinaga's,[21] but it has been extended by addition of two p functions with exponents 0.1142 and 0.0474 that are needed in order to represent the $5p$ orbital. In addition, the exponent of the most diffuse s function has been altered from 0.026341989 to 0.03, and that of the most diffuse d function from 0.10075175 to 0.1225. The primitive basis set $(17s,13p,8d)$ has been contracted to $(10s,8p,5d)$ using a segmented contraction scheme. In the contracted basis the $4d$ orbital is represented by a triple zeta function while all other orbitals including the unoccupied $5p$ orbital is represented by double zeta functions. For the C atom we have used Huzinaga's $(10s,6p)$ basis,[22] but augmented by a diffuse d function with exponent 0.75, as suggested by Dunning and Hay.[23] The basis set for the C atom has been contracted to $(4s,3p,1d)$ resulting in double zeta representation of the s functions, triple zeta representation of the $2p$ function, and a d polarization function.

In Table I we compare the calculated relative energies of the low-lying terms of the Y and the C atoms with the corresponding experimental values. For each atom the calculated ground term is in accordance with the experimental. For the Y atom it is, however, noted that the terms $^4F(4d)^2(5s)^1$ and $^4F(4d)^1(5s)^1(5p)^1$ are calculated to be appreciably lower than experimentally determined. This discrepancy has to be taken into account when interpreting the results of the present *ab initio* calculations, since it certainly will influence the calculated energy splittings of the electronic states of the YC molecule arising from the different orbital configurations of the Y atom.

The difference between the electronegativities of the atoms Y and C indicates that the YC molecule is likely to be appreciable polar with charge transfer from the Y to the C atom. As part of the YC molecule the resulting configuration of the Y atom is presumably somewhere in between the $(4d)^1(5s)^2$ of the neutral Y atom and $(4d)^1(5s)^1$ of the Y^+ ion. Another possibility for the Y atom is the $(4d)^2$ configuration, but for both the Y atom and the Y^+ ion terms originating from a $(4d)^2$ configuration are found at considerable higher energies, and therefore it seems likely that the electronic ground state of YC should be derivable from a configuration including just a single $4d$ electron. In consequence of the reasoning presented above, the configuration of C as part of YC is expected to be somewhere in between $(2p)^2$ and $(2p)^3$.

TABLE I. Relative energies (in a.u.) of the lowest lying terms of the Y and the C atoms as derived in HF calculations. Also included are the corresponding experimental values.

Atom	Term	Calculated	Experimental[a]
Y	$^2D(4d)^1(5s)^2$	0.000 000	0.000 000
Y	$^2P(5s)^2(5p)^1$	0.060 579	0.049 047
Y	$^4F(4d)^2(5s)^1$	0.017 773	0.049 933
Y	$^4P(4d)^2(5s)^1$	0.050 367	0.068 649
Y	$^2F(4d)^2(5s)^1$	0.053 022	0.069 783
Y	$^4F(4d)^1(5s)^1(5p)^1$	0.027 807	0.070 038
Y	$^2D(4d)^2(5s)^1$	0.058 816	0.071 875
C	$^3P(2s)^2(2p)^2$	0.000 000	0.000 000
C	$^1D(2s)^2(2p)^2$	0.057 377	0.046 311
C	$^1S(2s)^2(2p)^2$	0.139 455	0.098 502

[a]Center of gravity of each multiplet has been calculated from data of C. E. Moore, Natl. Bur. Stand. Circ. No. 467 (U.S. GPO, Washington, D.C. 1949 and 1952), Vols. 1 and 2.

Taking into account that the YC molecule has $C_{\infty v}$ symmetry, and just accounting for the one $4d$ and the two $5s$ electrons of Y and the two $2p$ electrons of C it appears likely that the electronic ground state of YC should arise from one of the valence shell configurations: $(\pi)^3(\sigma)^2$ or $(\pi)^2(\sigma)^2(\sigma')^1$, since the $4d\delta$ orbital of Y cannot contribute to the bonding of the YC molecule. Both these configurations, $(\pi)^3(\sigma)^2$ and $(\pi)^2(\sigma)^2(\sigma')^1$, should cause bonding due to the σ as well as the π orbitals. The configuration $(\pi)^3(\sigma)^2$ gives rise to just one state, i.e., $^2\Pi$. The configuration $(\pi)^2(\sigma)^2(\sigma')^1$ gives rise to the electronic states $^2\Sigma^+$, $^2\Sigma^-$, $^2\Delta$, and $^4\Sigma^-$. In Table II we present results of HF calculations of the $^2\Pi$ and of the $^4\Sigma^-$ states of the above configurations at the internuclear distance 3.6 a.u. It is noted that both these states are bound relative to the free atoms by 0.58 and 1.68 eV, respectively. In addition to these two states we present results for another two states with three π electrons, i.e., $^4\Pi(\pi)^3(\sigma)^1(\sigma')^1$ and $^4\Pi,\Phi(\pi)^3(\sigma)^1(\delta)^1$. From Table II, it is noted that both of these states are appreciably more stable than the state $^2\Pi(\pi)^3(\sigma)^2$; in fact, the $^4\Pi(\pi)^3(\sigma)^1(\sigma')^1$ state has the lowest energy of all the states investigated. We also performed HF calculations on three additional states with only two π electrons, i.e., the states $^6\Delta(\pi)^2(\sigma)^1(\sigma')^1(\delta)^1$, $^4\Delta(\pi)^2(\sigma)^2(\delta)^1$, and $^6\Sigma^+(\pi)^2(\sigma)^1(\delta)^2$. In addition to the above mentioned, we have performed HF calculations on

TABLE II. Total energies for the YC molecule as resulting from HF calculations at the internuclear distance 3.6 a.u. Also included are the dipole moments, the gross atomic charge, as well as the number of s and d electrons on Y.

State	Valence shell configuration					Energy[a] (a.u.)	Gross atomic charge on Y	Total number of d electrons on Y	Occupation of Y orbitals				Dipole moment (D)
	10σ	11σ	12σ	5π	1δ				$4d\sigma$	$4d\pi$	$4d\delta$	$5s$	
$^4\Pi$	2	1	1	3	0	−0.083 384	0.71	11.26	0.40	0.86	0.00	0.78	1.69
$^6\Delta$	2	1	1	2	1	−0.071 724	0.62	11.53	0.32	0.22	1.00	0.80	0.77
$^4\Sigma^-$	2	2	1	2	0	−0.061 896	0.66	11.26	0.83	0.43	0.00	0.82	1.92
$^4\Pi,\Phi$[b]	2	1	0	3	1	−0.034 556	0.78	12.10	0.34	0.77	1.00	0.04	3.43
$^2\Sigma^+$	2	1	0	4	0	−0.025 188	0.66	11.93	0.64	1.29	0.00	0.32	3.51
$^2\Pi$	2	2	0	3	0	−0.019 222	0.64	11.97	1.05	0.92	0.00	0.10	3.69
$^4\Delta$	2	2	0	2	1	−0.008 898	0.70	12.09	0.70	0.39	1.00	0.04	3.21
$^6\Sigma^+$	2	1	0	2	2	0.011 278	0.63	12.42	0.22	0.21	2.00	0.00	2.04
$^2\Delta$	2	0	0	4	1	0.018 298	0.74	12.18	0.10	1.08	1.00	0.03	
$^2\Pi$	2	2	2	1	0	0.038 985	0.49	10.83	0.70	0.13	0.00	1.62	0.49
$^4\Pi,\Phi$[b]	2	2	1	1	1	0.047 486	0.50	11.63	0.51	0.12	1.00	0.81	1.01
$^4\Pi$	2	2	0	1	2	0.130 213	0.51	12.50	0.39	0.11	2.00	0.00	2.06

[a]Energy of YC minus energy of the Y $^2D(4d)^1(5s)^2$ and the C $^3P(2s)^2(2p)^2$.
[b]The wave function represents a mixture of orbital angular momenta.

two states with four π electrons, $^2\Sigma^+(\pi)^4(\sigma)^1$ and $^2\Delta(\pi)^4(\delta)^1$, and three states with only one π electron, i.e., $^2\Pi(\pi)^1(\sigma)^2(\sigma')^2$, $^4\Pi,\Phi(\pi)^1(\sigma)^2(\sigma')^1(\delta)^1$, and $^4\Pi(\pi)^1(\sigma)^2(\delta)^2$.

Table II shows selected results of all the HF calculations performed. It is noted that seven of the states considered are bound relative to the free HF atoms. Furthermore, all the states investigated are polar with sizeable charge transfer from Y to C. However, since the states arise from different orbital configurations of the Y atom, the HF energies do not provide accurate relative energies of these states. The lowest lying state identified in the HF calculations is $^4\Pi$. However, the correlation energy is expected to be larger in the doublet states than in the quartet state, and therefore it is not justified to predict the ground state of the YC molecule as being $^4\Pi$ on basis of the the HF results. On this background we decided to perform further investigations of the low-lying electronic states of the YC molecule by carrying out MCSCF calculations within the framework of CASSCF.

B. CASSCF calculations on the YC molecule

In the CASSCF calculations the core orbitals, i.e., the $1s$, $2s$, $3s$, $4s$, $2p$, $3p$, $4p$, and $3d$ of Y and the $1s$ orbital of C, were kept fully occupied. The valence orbitals occupied in the atoms, i.e., $5s$ and $4d$ of Y and $2s$ and $2p$ of C, were included in the active space. The CASSCF calculations have been performed for doublet, quartet, and sextet states of the space symmetries Σ^+, Σ^-, and Π. The number of configurations included in the CASSCF calculations reached 1536 for the doublet states, 952 for the quartet states, and 192 for the sextet states.

The CASSCF calculations have been performed as functions of the internuclear distance, i.e., for the distances 3.6, 3.9, 4.2, 5.0, and 12.0 a.u. For the doublet and quartet states an additional point was included at 3.3 a.u. The resulting potential energy curves are shown in Fig. 1. Table III shows the spectroscopic constants obtained by fitting the potential energies as derived in the CASSCF calculations to Morse curves. The results obtained for the $^4\Sigma^+$ state are not included, since this state turned into a mixture of the states $^4\Sigma^+$ and $^4\Delta$ in the course of the calculations. In Table IV the populations of the natural valence orbitals are shown for the low-lying electronic states of the YC molecule at the internuclear distance 3.9 a.u.

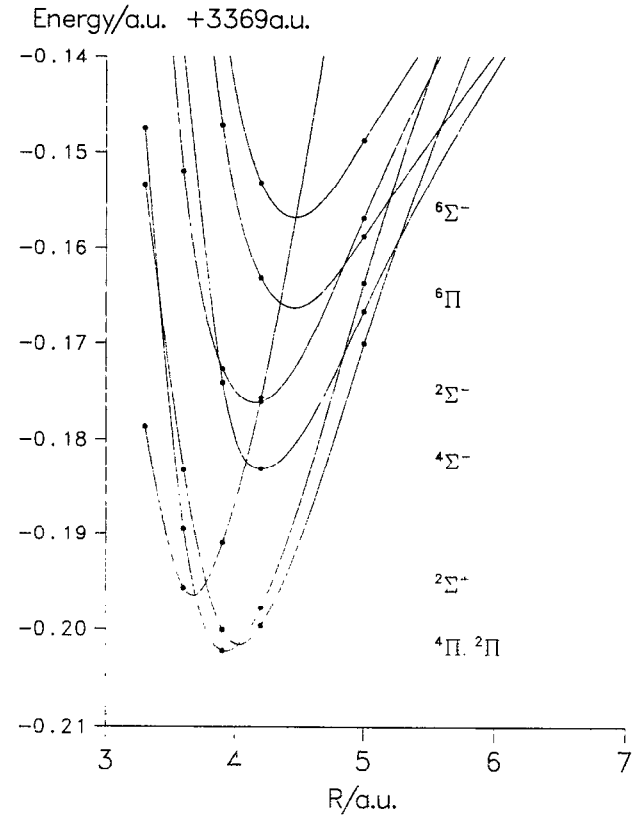

FIG. 1. Potential energy curves of 7 low-lying electronic states of the YC molecule as derived in CASSCF calculations.

TABLE III. Spectroscopic constants of the low-lying electronic states, as derived in CASSCF calculations.

State	Equilibrium distance (a.u.)	Vibrational frequency (cm^{-1})	Transition energy (cm^{-1})	Dissociation energy[a] (eV)
$^4\Pi$	3.95	651	0	2.97
$^2\Pi$	4.03	586	225	
$^2\Sigma^+$	3.66	719	1393	
$^4\Sigma^-$	4.24	531	4215	
$^2\Sigma^-$	4.14	511	5744	
$^6\Pi$	4.47	449	7826	
$^6\Sigma^-$	4.48	473	9887	
$^6\Sigma^+$	4.74	325	23304	

[a]Derived as the difference between the total molecular energy at the equilibrium distance and at the internuclear distance 12.0 a.u.

From Fig. 1 and Table III it is observed that the predicted electronic ground state of the YC molecule is $^4\Pi$, but this state is calculated to be only 225 cm^{-1} more stable than the first excited state, $^2\Pi$, and 1393 cm^{-1} more stable than the $^2\Sigma^+$ state. In view of these results the prediction of the electronic ground state of YC as being $^4\Pi$ is rather uncertain. Especially because the two higher-lying states are doublet states, which are expected to have larger correlation energies than the quartet state. There are, however, several factors that support the assignment of $^4\Pi$ as being the electronic ground state of the YC molecule. Thus, Table IV shows that the two lowest lying states, $^4\Pi$ and $^2\Pi$, arise from similar orbital configurations. This suggests that their correlation energies are also similar. Furthermore, the next higher lying state, $^2\Sigma^+$, is due to the excited configuration $(4d)^2(5s)^1$ of the Y atom, and the results presented in Table I shows that atomic terms of this orbital configuration have smaller correlation energies than the terms arising from the atomic ground term configuration $(4d)^1(5s)^2$ of Y. These atomic correlation problems certainly are carried over into the molecular calculations, presumably resulting in too low relative energy of the $^2\Sigma^+$ state as compared to that of the $^4\Pi$ state. Therefore, on basis of the present work, we are confident to predict the symmetry of the electronic ground state of the YC molecule as being either $^4\Pi$ or $^2\Pi$. Recently, however, the YC molecule has been investigated spectroscopically in the gas phase,[24] and the ground state has been assigned $\Omega=5/2$. A Ω of 5/2 cannot be due to either of the states, $^2\Pi$ or $^2\Sigma^+$, but $\Omega=5/2$ is consistent with an electronic ground state of $^4\Pi$. The combination of the theoretical and the experimental investigations of the YC molecule thus yields the result that the electronic ground state of YC is $^4\Pi$.

From Table IV, it is noted that the two lowest-lying electronic states, $^4\Pi$ and $^2\Pi$, both have approximately three π and two σ valence electrons, not considering the electrons in the 10σ orbital which are basically the 2*s* electrons of C. Contrary to our expectations, the two σ electrons in the $^2\Pi$ state do not pair up in just one molecular orbital, but rather occupy two different orbitals. This presumably is the reason for the YC molecule having a $^4\Pi$ and not a $^2\Pi$ electronic ground state. Thus, the energy difference in between the states $^4\Pi$ and $^2\Pi$ is a measure of the different exchange couplings in the two states. Just like the states $^4\Pi$ and $^2\Pi$, the state $^6\Pi$ has three π and two σ valence electrons. The higher energy of the $^6\Pi$ state as compared to the states $^4\Pi$ and $^2\Pi$ is in accordance with one π electron occupying an anti bonding molecular orbital in the $^6\Pi$ state.

The low lying $^2\Sigma^+$ state has approximately four π and one σ valence electrons. The $^4\Sigma^-$, $^2\Sigma^-$, and $^6\Sigma^-$ states all have two π and three σ valence electrons. Although the 11σ orbital contains approximately two electrons in the states $^4\Sigma^-$ and $^2\Sigma^-$, these states do have considerably higher energy than the states $^4\Pi$ and $^2\Pi$, indicating that the formation of the π bonds are more important for the bonding in this molecule than the formation of the σ bonds.

TABLE IV. Energies and populations of the natural valence orbitals in the low lying electronic states of YC as derived in CASSCF calculations at the internuclear distance 3.9 a.u.

State	Energy (eV)	Occupation					
		10σ	11σ	12σ	13σ	5π	6π
$^4\Pi$	0.00	1.97	1.00	0.99	0.03	2.88	0.13
$^2\Pi$	0.06	1.97	1.32	0.68	0.02	2.87	0.14
$^2\Sigma^+$	0.30	1.96	0.97	0.05	0.02	3.81	0.19
$^4\Sigma^-$	0.77	1.99	1.82	1.00	0.01	2.00	0.18
$^2\Sigma^-$	0.80	1.98	1.87	1.00	0.13	1.96	0.06
$^6\Pi$	1.50	1.98	1.00	1.00	0.01	2.00	1.01
$^6\Sigma^-$	1.83	1.98	1.00	1.00	1.00	2.00	0.02
$^6\Sigma^+$	3.76	1.95	1.00	0.04	0.00	2.00	2.00

TABLE V. The major contributions to the CASSCF wave function describing the low-lying electronic states $^4\Pi$, $^2\Pi$, and $^2\Sigma^+$, of the YC molecule as functions of the internuclear distance.

	Valence shell configuration						Contribution of valence shell configuration (%)					
							Internuclear distance (a.u.)					
State	10σ	11σ	12σ	13σ	5π	6π	3.3	3.6	3.9	4.2	5.0	12.0
$^4\Pi$	2	1	1	0	3	0	94	93	91	88	45	
	2	2	0	0	2	1					20	93
	2	1	1	0	2	1			1	1	10	
	2	0	2	0	2	1					9	4
	2	1	1	0	1	2	2	3	4	5	13	
	2	1	0	1	2	1	1	1	1			
	0	2	0	2	2	1						2
$^2\Pi$	2	2	0	0	3	0	91	41	53	56	41	34
	2	1	1	0	3	0		21	15	13	11	
	2	0	2	0	3	0	2	30	22	19	13	1
	2	2	0	0	2	1				1	7	23
	2	1	1	0	2	1	2		1	2	8	
	2	2	0	0	1	2	2	1	2	3	8	34
	2	0	2	0	1	2		1	1	2	4	1
$^2\Sigma^+$	2	1	0	0	4	0	91	89	87	85	61	12
	2	1	0	0	3	1					8	17
	2	0	1	0	3	1	1	2	3	3	1	
	2	1	0	0	2	2	3	4	6	7	23	41
	2	1	0	0	0	4						3
	2	1	0	0	1	3						1

The highest-lying electronic state considered is $^6\Sigma^+$. This state has four π and one σ valence electrons. The π electrons are distributed with two electrons in the bonding and two in the antibonding molecular orbital. This is consistent with our findings that this state is hardly bound at all.

C. The lowest lying electronic states of YC

Table V shows the contributions of the major configurations of the wave functions as functions of the internuclear distance for the three lowest-lying electronic states, $^4\Pi$, $^2\Pi$, and $^2\Sigma^+$. It is noted that the states $^4\Pi$ and $^2\Sigma^+$ have just one leading configuration at internuclear distances in between 3.3 and 4.2 a.u., i.e., $(10\sigma)^2(11\sigma)^1(12\sigma)^1(5\pi)^3$ for $^4\Pi$ and $(10\sigma)^2(11\sigma)^2(5\pi)^4$ for $^2\Sigma^+$. At internuclear distances 3.6 to 4.2 a.u. the $^2\Pi$ state, on the other hand, has considerable weights on three configurations, $(10\sigma)^2(11\sigma)^2(5\pi)^3$, $(10\sigma)^2(12\sigma)^2(5\pi)^3$, and $(10\sigma)^2(11\sigma)^1(12\sigma)^1(5\pi)^3$. The three major configurations in the $^2\Pi$ state are precisely those required to localize the σ electrons.

In the present work we have analyzed the electronic wave functions by carrying out Mulliken population analyses. The results of such analyses are of course only qualitative, but we still consider it a convenient way of translating the electronic wave functions into a chemical language.

The Mulliken population analyses of the natural orbitals of the three low-lying electronic states show that there are distinct differences between the σ and the π valence orbitals. The π valence orbitals are ordinary bonding and antibonding molecular orbitals. Thus, the 5π orbital is the bonding combination of the Y $4d\pi$ and the C $2p\pi$, while the 6π orbital is the corresponding antibonding combination. The σ orbitals, on the other hand, remain essentially localized and nonbonding. Accordingly the total overlap populations are mainly due to the π orbitals for all three low-lying states.

Closer analyses of the natural orbitals of the low-lying states $^4\Pi$ and $^2\Pi$ reveal the reason for the σ orbitals being nonbonding. Thus, the 10σ orbital is mainly the $2s$ orbital of C with just a slight admixture of the $4d\sigma$ orbital of Y. The 11σ orbital is a bonding combination of the $2p\sigma$ orbital of C and a $5s,5p\sigma$ hybrid orbital of Y, but the latter is polarized away from the internuclear region. The 12σ orbital is the antibonding combination of the $2p\sigma$ of C and the $5s$ of Y, but with some contribution also from the $4d\sigma$ of Y. Thus, altogether the σ orbitals cause the charge to be removed from the internuclear region.

The YC molecule is polar with a substantial charge transfer from the Y to the C atom. In the states $^4\Pi$ and $^2\Pi$, the charge transfer give rise to dipole moments of 3.90 D in the $^4\Pi$ ground state and of 2.72 D in the $^2\Pi$ state.

Figures 2, 3, and 4 show the analyses of the wave functions in terms of populations of the individual atomic orbitals as functions of the internuclear distance for the three low-lying electronic states, $^4\Pi$, $^2\Pi$, $^2\Sigma^+$.

Figures 2 and 3 are very much alike, showing the similarity between the states $^4\Pi$ and $^2\Pi$. At 12 a.u. the configuration of the C atom is basically $(2p\pi)^2$ and that of the Y atom is $(4d\pi)^1(5s)^2$. As the atoms approach each other approximately one electron is transferred from the $5s$ orbital of Y into the $2p\sigma$ orbital of C. At internuclear distances shorter than the equilibrium distance of the mole-

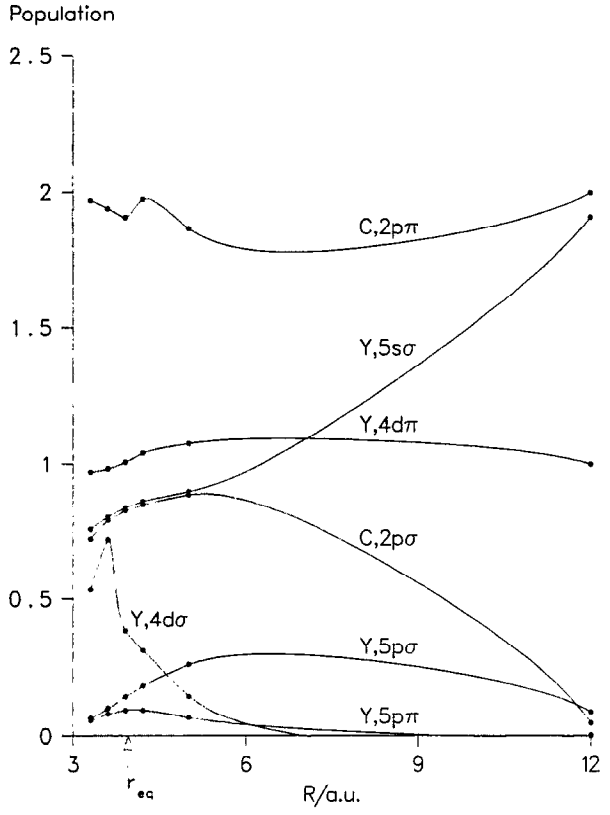

FIG. 2. Populations associated with the valence orbitals of the atoms Y and C in the $^4\Pi$ electronic ground state of YC as derived from CASSCF wave functions. The equilibrium distance of the state is indicated by r_{eq}.

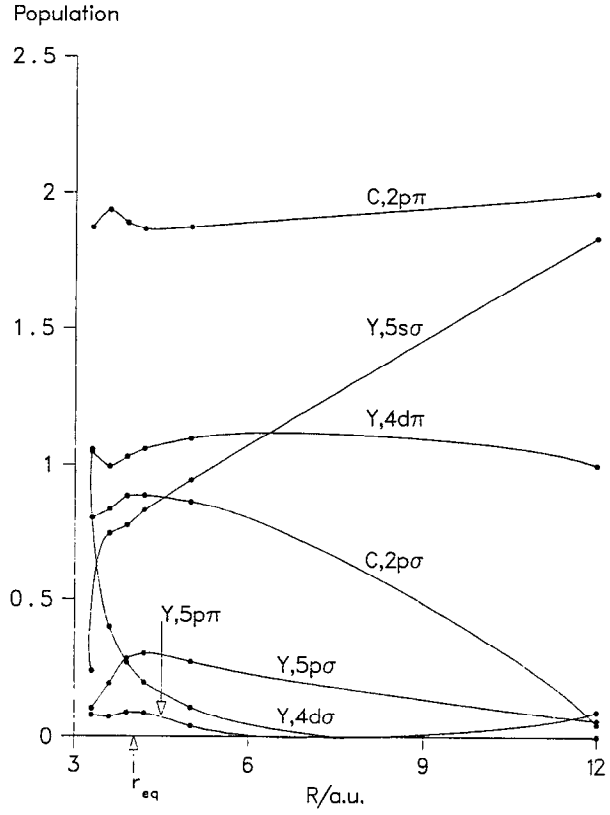

FIG. 3. Populations associated with the valence orbitals of the atoms Y and C in the $^2\Pi$ electronic state of YC as derived from CASSCF wave functions. The equilibrium distance of the state is indicated by r_{eq}.

cule the $4d\sigma$ orbital of Y acquires significant population.

From Figure 4 it is recognized that the interaction leading to the $^2\Sigma^+$ state of the YC molecule occurs between a C atom with configuration $(2p\pi)^2$ and a Y atom with the excited term configuration $(4d\pi)^2(5s)^1$. As the atoms approach each other an electron appears to jump from the $5s$ orbital of Y into the $2p\sigma$ orbital of C. It is noted that there is substantial redistribution of charge as the internuclear distance is diminished below 5 a.u.

Figure 5 shows the dipole moments of the three low-lying electronic states, $^4\Pi$, $^2\Pi$, and $^2\Sigma^+$, as derived from the CASSCF wave functions and as functions of the internuclear distances. The sharp dip in the dipole moment of the $^2\Sigma^+$ state at 4.2 a.u. reflects the changes in the orbital configuration of the Y and the C atoms as noted in Fig. 4.

The low-lying electronic states of the YC molecule will of course split due to the spin–orbit coupling, but the splittings will be small, since the spin–orbit coupling constants, as derived from Moore's tables, amount to only 212.14 cm^{-1} for the $^2D(4d)^1(5s)^2$ term of Y, and to 237.34 cm^{-1} for the $^3D(4d)^1(5s)^1$ term of Y^+. Furthermore, a simple perturbation treatment of the spin–orbit coupling indicates that the states with $\Omega=5/2$, 3/2, and 3/2 obtained from the $^4\Pi$ state will remain approximately degenerate. Therefore, we have chosen to utilize the energies of the electronic states, as derived in the CASSCF wave functions to evaluate the partition function necessary for deriving the dissociation energy of the YC molecule from the mass spectrometric data described in the following section.

III. MASS SPECTROMETRIC INVESTIGATIONS

A. Mass spectrometric measurements

The description of the high temperature mass spectrometer, the experimental technique and the procedure have been given elsewhere.[25,26] A graphite cell was placed in an outer tantalum Knudsen cell and charged with yttrium, iridium, and carbon powder in the molar ratio 3:1:15. About 20 mg of gold was added for the purpose of instrument calibration. The cells had concentric orifices of 1 mm diameter, and they were heated by radiation from a tungsten resistance heater. The temperature was measured by a calibrated optical pyrometer. A 19 V electron beam was used to ionize the molecular species effusing from the Knudsen cell. The species observed in the course of the experiment and pertinent to this paper were $Y^+(89)$, $YC^+(101)$, and $YC_2^+(113)$. In the same investigation, the yttrium carbides, YC_n, $n=2$–8,[27] diyttrium carbides, Y_2C_n, $n=2$–8,[28] and the mixed yttrium–iridium carbides, $YIrC_n$, $n=1$–2,[25] as well as the intermetallic molecules, YAu and YIr[29] were also detected. All the ions were identified by their mass to charge ratio, shutter profiles and appearance potentials. In Table VI,[30] we report the isotopic intensities of the ions, measured in the temperature range 2365–2792

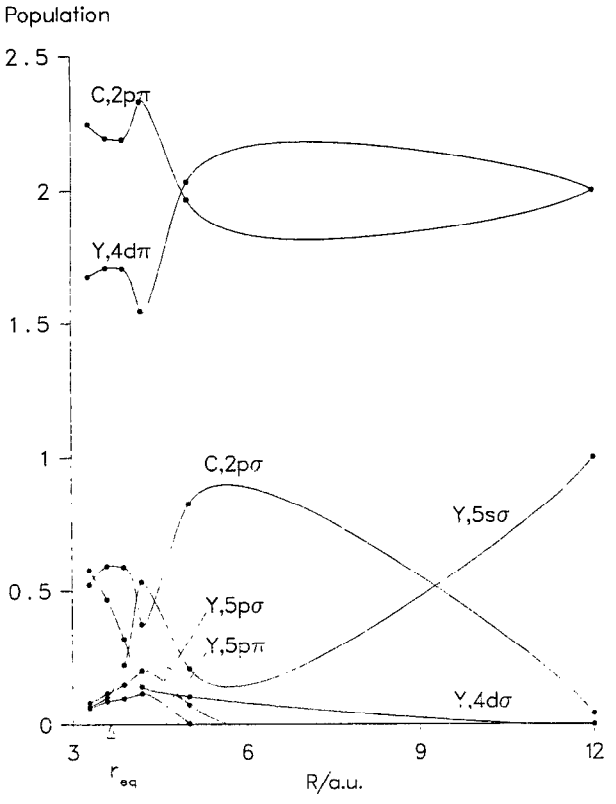

FIG. 4. Populations associated with the valence orbitals of the atoms Y and C in the $^2\Sigma^+$ electronic state of YC as derived from CASSCF wave functions. The equilibrium distance of the state is indicated by r_{eq}.

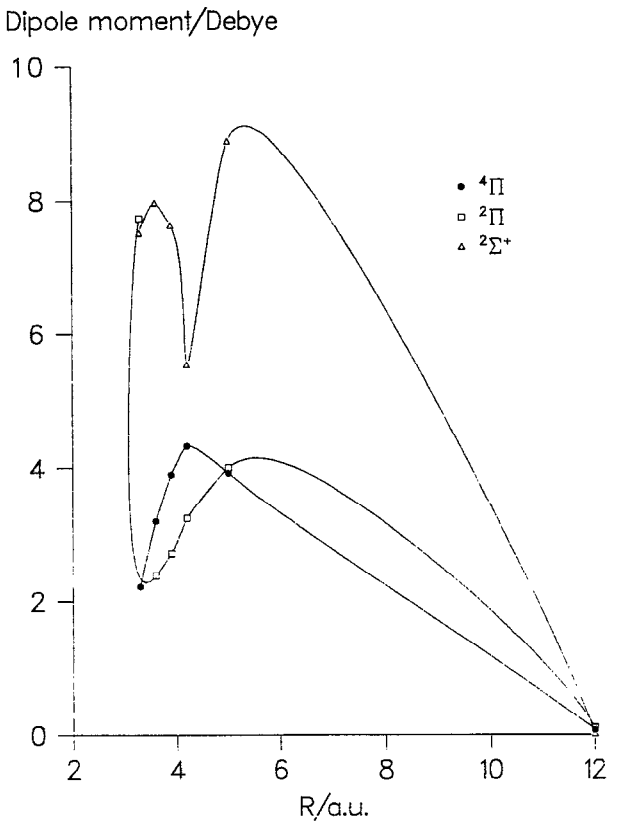

FIG. 5. Dipole moments of the three low-lying electronic states, $^4\Pi$, $^2\Pi$, and $^2\Sigma^+$, of the YC molecule as derived from CASSCF wave functions.

K. The appearance potentials were measured as 6.4±0.5 for Y^+, 8.5±2.0 for YC^+, and 6.9±0.5 eV for YC_2^+, using the appearance potential of gold, as in Ref. 31.

Several ionization efficiency curves of YC^+ were measured at different temperatures in order to evaluate the contribution to the intensity of this ion arising from fragmentation of higher species, mainly YC_2. Only about 4.6% of the YC^+ intensity resulted from the ionization of the primary specie, and the remainder of the YC^+ measured corresponds to 1.1% fragmentation of the YC_2 in the temperature range investigated. Analogous factors of fragmentation have been obtained in previous experiments carried out in our laboratory when studying the gaseous UC[32] and CeC[33] molecules. Therefore, at each experimental temperature 1.1% of the YC_2^+ intensity was subtracted from the intensity of YC^+. The resulting values are listed in Table VI. The method of the pressure calibration used has been described previously.[25] The pressure constants for Y, YC, and YC_2 were obtained as 0.580, 0.916, and 0.582 atm A^{-1} K^{-1}, respectively.

B. Thermodynamic evaluation of data and results

The second law and the third law methods were employed to evaluate the enthalpies of the following equilibrium reactions

$$Y(g)+C(\text{graph.})=YC(g), \quad (1)$$

$$Y(g)+YC_2(g)=2\ YC(g). \quad (2)$$

Details on the thermochemical evaluation of the experimental data are given elsewhere.[27] The unit activity of carbon in the Knudsen cell, required in the thermodynamic evaluation of reaction (1), was ensured by the inner cell and the excess graphite powder. The Gibbs energy function, $(G_T^\circ - H_\Theta^\circ)/T$, and heat content functions, $(H_T^\circ - H_\Theta^\circ)$, $\Theta=0$, or 298.15 K, necessary for evaluating the enthalpy of the reaction, were taken from literature for Y(g) and C(graph.).[34] For YC the corresponding functions were evaluated using the experimental spectropic data for the electronic ground state, $r_e=2.05$ Å and $\omega_e=686\ \text{cm}^{-1}$,[24] combined with our calculated energy levels. The resulting values are listed in Table VII for 0 K reference temperature. The corresponding values for the YC_2

TABLE VII. Gibbs energy functions $-(G_T^\circ - H_0^\circ)/T$, in J K^{-1} mol^{-1} and heat content functions, $H_T^\circ - H_0^\circ$, in kJ mol^{-1} for gaseous YC.

T, K	$-(G_T^\circ - H_0^\circ)/T$	$H_T^\circ - H_0^\circ$
298.15	217.2	9.42
2200	286.3	82.29
2400	289.6	90.41
2600	292.6	98.58
2800	295.4	106.81
3000	298.0	115.08

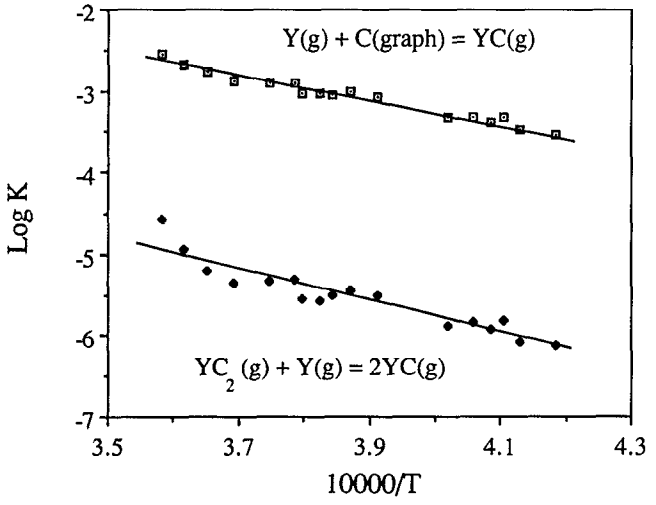

FIG. 6. Log K vs 1/T for the reactions $Y(g)+C(graph.)=YC(g)$ and $YC_2(g)+Y(g)=2YC(g)$.

molecule have been reported elsewhere.[27] In Fig. 6 the second law plots of reactions (1) and (2) are shown.

Table VIII[30] shows the detailed third-law evaluation for reaction (1). The associated error is the standard deviation from the mean. In Table IX the enthalpies for the reactions (1) and (2) obtained with the second and third law methods have been summarized. Here the error terms correspond to the standard deviation. In evaluating the selected values of the reaction enthalpies, double weight was given to the respective third law values. The associated errors have been calculated from an overall estimation of the uncertainties relative to the experimental technique and assumptions made in the evaluation of the data.

From reaction (1) the dissociation energy obtained using $\Delta H^\circ_{v,0}(graph.)=711.2\pm2.1$ kJ mol^{-1} or $\Delta H^\circ_{v,298.15}(graph.)=716.7\pm2.1$ kJ mol^{-1},[34] is $D^\circ_0(YC)=414.9\pm14$ kJ mol^{-1}, and $D^\circ_{298.15}(YC)=418.9\pm14$ kJ mol^{-1}. From reaction (2) with $\Delta H^\circ_{a,0}(YC_2)=1225\pm8$ kJ mol^{-1},[27] we derive $D^\circ_0(YC)=412.9\pm16$ kJ mol^{-1}. Likewise $\Delta H^\circ_{a,298.15}(YC_2)=1235\pm8$ kJ mol^{-1} [27] yields $D^\circ_{298.15}(YC)=417.2\pm16$ kJ mol^{-1}. The standard heat of formation of YC, $\Delta H^\circ_{f,298.15}$ is derived from reaction (1) as 708.1 ± 16 kJ mol^{-1} using $\Delta H^\circ_{v,298.15}(Y)=424.7\pm2.1$ kJ mol^{-1}.[34]

TABLE IX. Summary of second-law and third-law enthalpies of the reactions $Y(g)+C(graph.)=YC(g)$ (1) and $Y(g)+YC_2(g)=2YC(g)$ (2). All values are in kJ mol^{-1}.

Method	Property	Reaction (1)	Reaction (2)
2nd law	ΔH°_{2575}	276.5 ± 12.7	377.6 ± 35.7
	ΔH°_0	288.0	388.5
	$\Delta H^\circ_{298.15}$	289.4	389.8
3rd law	ΔH°_0	300.4 ± 2.5	404.8 ± 6.9
	$\Delta H^\circ_{298.15}$	301.9	406.1
	ΔH°_0, selected	296.3 ± 12	399.3 ± 24
	$\Delta H^\circ_{298.15}$, selected	297.8	400.7

The selected dissociation energy of YC, $D^\circ_0=414.2\pm14$ kJ mol^{-1} was obtained by giving twice the weight to reaction (1). It compares well with the corresponding values for CeC, 441 ± 12 kJ mol^{-1},[33] and for LaC, 458.3 ± 20 kJ mol^{-1},[35] and it is in agreement with the previously proposed value by Gingerich, 414 ± 63 kJ mol^{-1}.[36] This trend in the dissociation energies of the monocarbides corresponds to the analogous trend in the M–C_2 bond strengths, i.e., $D^\circ_0(Y\text{–}C_2)=627\pm20$ kJ mol^{-1},[27] $D^\circ_0(La\text{–}C_2)=665\pm25$ kJ mol^{-1},[37] and $D^\circ_0(Ce\text{–}C_2)=670\pm20$ kJ mol^{-1}.[33]

IV. CONCLUSIONS

In the present work, we have reported results of theoretical as well as experimental investigations of the YC molecule. The electronic structure and the nature of the bonding in the YC molecule have been elucidated through all electron MCSCF (CASSCF) calculations. The dissociation energy of the YC molecule has been derived from the data obtained in the high temperature equilibrium mass spectrometric measurements in combination with the calculated electronic states.

The electronic ground state of the YC molecule has been calculated as being $^4\Pi$, but this state is separated from the next higher-lying state, $^2\Pi$, by only 225 cm^{-1}, and by 1393 cm^{-1} from the $^2\Sigma^+$ state. Although the energy splittings of the low-lying electronic states of the YC molecule are calculated to be small, detailed analyses of the wave functions support the ground state assignment, $^4\Pi$. In addition, recent spectroscopic investigations[24] have determined that the ground state of the YC molecule has $\Omega=5/2$. Considering only the three low-lying states, $^4\Pi$, $^2\Pi$, and $^2\Sigma^+$, a $\Omega=5/2$ is consistent only with $^4\Pi$ being the electronic ground state.

In all the low-lying electronic states investigated the main bonding orbitals are the valence π orbitals. The molecular valence σ orbitals are essentially nonbonding, although they are bonding combinations of the σ orbitals located on the individual atoms. They are nonbonding, because the atomic orbitals making up the molecular orbitals are polarized away from the internuclear region.

The YC molecule is appreciably polar with charge transfer from the Y to the C atom. The chemical bond presumably occurs by a harpooning mechanism. At some distance in between 12 and 5 a.u. an electron is transferred from the Y to the C atom, and this enables the formation of the chemical bond between the $4d\pi$ electron on Y and the $2p\pi$ electrons on C.

Our calculated dissociation energy amounts to 2.97 eV, and the dissociation energy we have obtained in our mass spectrometric investigations is $D^\circ_0=414.2\pm14$ kJ mol^{-1} or 4.29 ± 0.15 eV. This deviation is according to our expectations when considering the amount of correlation included in the present calculations. The weaker bond in the YC molecule as compared to those of RhC and RuC is in agreement with our findings that of the electrons of Y, it is

essentially only the single $4d$ electron that is involved in the formation of the chemical bond in the YC molecule.

ACKNOWLEDGMENTS

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